



U.S. Department of Energy  
Energy Efficiency and Renewable Energy

*biomass program*

# Gasification of Biorefinery Residues

**DOE OBP Thermochemical Platform Review Meeting  
June 7-8, 2005**

**David C. Dayton  
National Renewable Laboratory**



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- **Project Background**
- **Project Overview**
  - Stage Placement
  - Objective
  - Milestones
- **Technical Feasibility and Risks**
- **History and Accomplishments**
- **Plan/Schedule**
- **Critical Issues and Show-stoppers**
- **Summary**



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Gas cleanup requirements will be dictated by biorefinery residue compositions that are a function of feedstock and pretreatment/process conditions

**Barriers Addressed:** Reducing Integrated Biorefinery product costs by defining a higher-value use for lignin-rich residues and off-spec biochemical conversion feedstocks

## Gas Cleanup Impacts

	N	S	Cl	Alkali	Tars	Syngas Quality
<i>Corn Fiber</i>	<i>M-H</i>	<i>L</i>	<i>L</i>	<i>L</i>	<i>?</i>	<i>?</i>
<i>DDGS</i>	<i>H</i>	<i>M</i>	<i>M</i>	<i>M</i>	<i>?</i>	<i>?</i>
Corn Fiber	M-H	L	L	L	?	?
Lignin*	M	L	M-H	M-H	?	?
Others...						

\*Depends on pretreatment and process conditions



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## Stage Placement – Stage A

Supports other projects and provides information for the design and operation of pilot-scale systems and technoeconomic analyses

## Project Objective

To ensure that biomass gasification technologies are compatible with the production of fuels and chemicals based on technologies currently available to facilitate the development of a vigorous industry based on biorefinery concepts to produce liquid transportation fuels and chemicals from biomass.

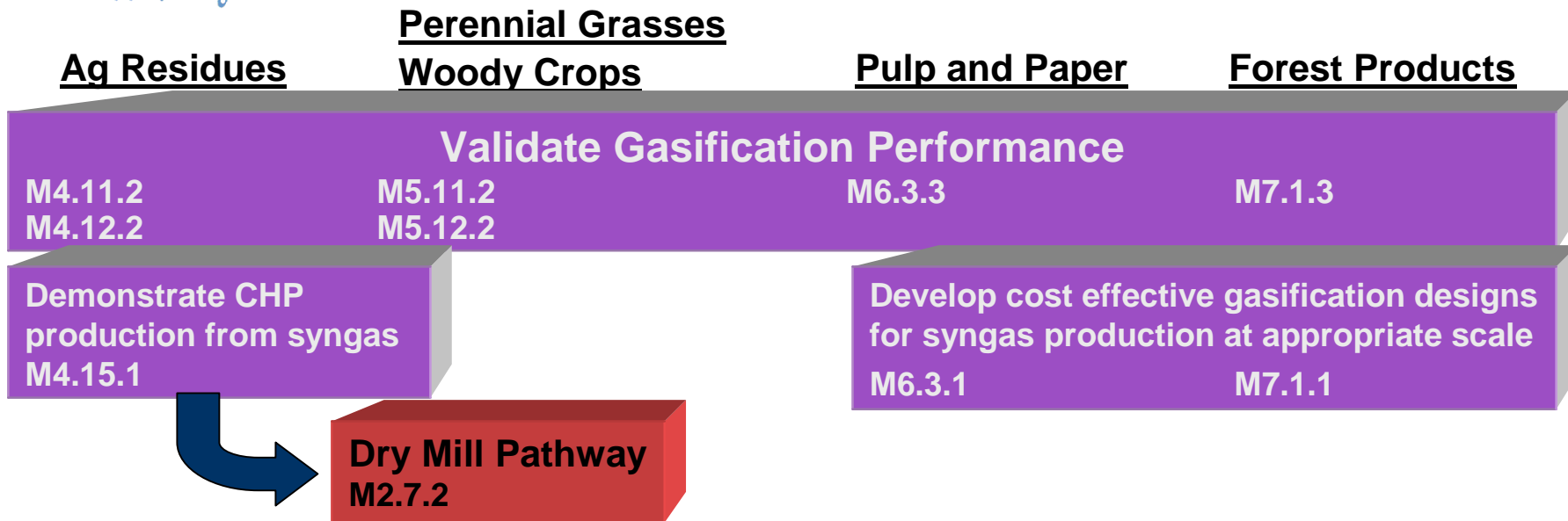
## Effect of Gasification Processing on Biochemical Conversion Residues Composition

Benchmark parametric corn stover gasification studies in NREL TCPDU with a new feedstock to evaluate syngas quality for Integrated Catalyst Studies Task.



# Pathways and Milestones – C-level and Project Milestones

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Project Milestones	Type	Performance Expectations	Due Date
Syngas Quality from Gasification of Biorefinery Residues	D	Identify key process and operating parameters that control tar formation and potential product selectivity by measuring selected biorefinery residues	Sept. 2005



# Technical Feasibility and Risks

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- Bench-scale and Pilot-scale studies provide fundamental data for relatively low cost and low risk
- Can explore a wide range of experimental conditions in a reasonable time frame to focus process optimization of demonstration projects
- Challenge: Develop correlations that apply to larger-scale systems



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## Gasification vs. Combustion of Lignin-rich Residues

- Improved efficiency of biomass utilization
- Higher liquid fuel yields per biomass input
- Improved CHP production efficiency
- Syngas as a natural gas replacement



# History and Accomplishments

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- Builds on past bench-scale studies
- Collected 14 representative residues/feedstocks
  - 10 corn stover varieties
  - Corn stover used in TCPDU studies
  - Wheat straw
  - NREL Corn Stover Biochemical Conversion Residue (lignin)
  - Forest residue
- Fuel analyses being completed for all collected samples
- Parametric Corn Stover Gasification in NREL TCPDU
  - 7 tons corn stover from Imperial, NE (S. Thomas NREL)
  - Pelletized by Sebs Feed and Supply in Tarreton, ID (R. Hess INL)





# Feedstock Fuel Variability

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Feedstock Composition			
	Wood	Corn Stover	BioChem Residue
Proximate Analysis (wt %)			
Moisture	3.74	5.78	0 (63.76)
Ash	0.63	10.69	14.02
Volatiles	82.68	67.35	60.25
Fixed C	12.95	16.18	25.73
Ultimate Analysis (wt%)			
C	51.36	44.0	55.95
H	6.25	4.68	5.20
N	0.11	0.68	2.27
O	37.89	34.09	22.37
S	0.02	0.08	0.19

NREL TCPDU Syngas Composition (S/B = 1)			
Vol%	Wood	Corn Stover	BioChem Residue
H <sub>2</sub>	28.1	25.4	?
CO	25.5	23.4	?
CO <sub>2</sub>	25.2	22.5	?
CH <sub>4</sub>	15.3	14.5	?
C <sub>2</sub> H <sub>4</sub>	3.7	4.4	?
Benzene (mg/Nm <sup>3</sup> )	6,500	10,000	?



# NREL's Thermochemical Process Development Unit (TCPDU)

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**On-line, Real-time  
Product Gas Analysis**

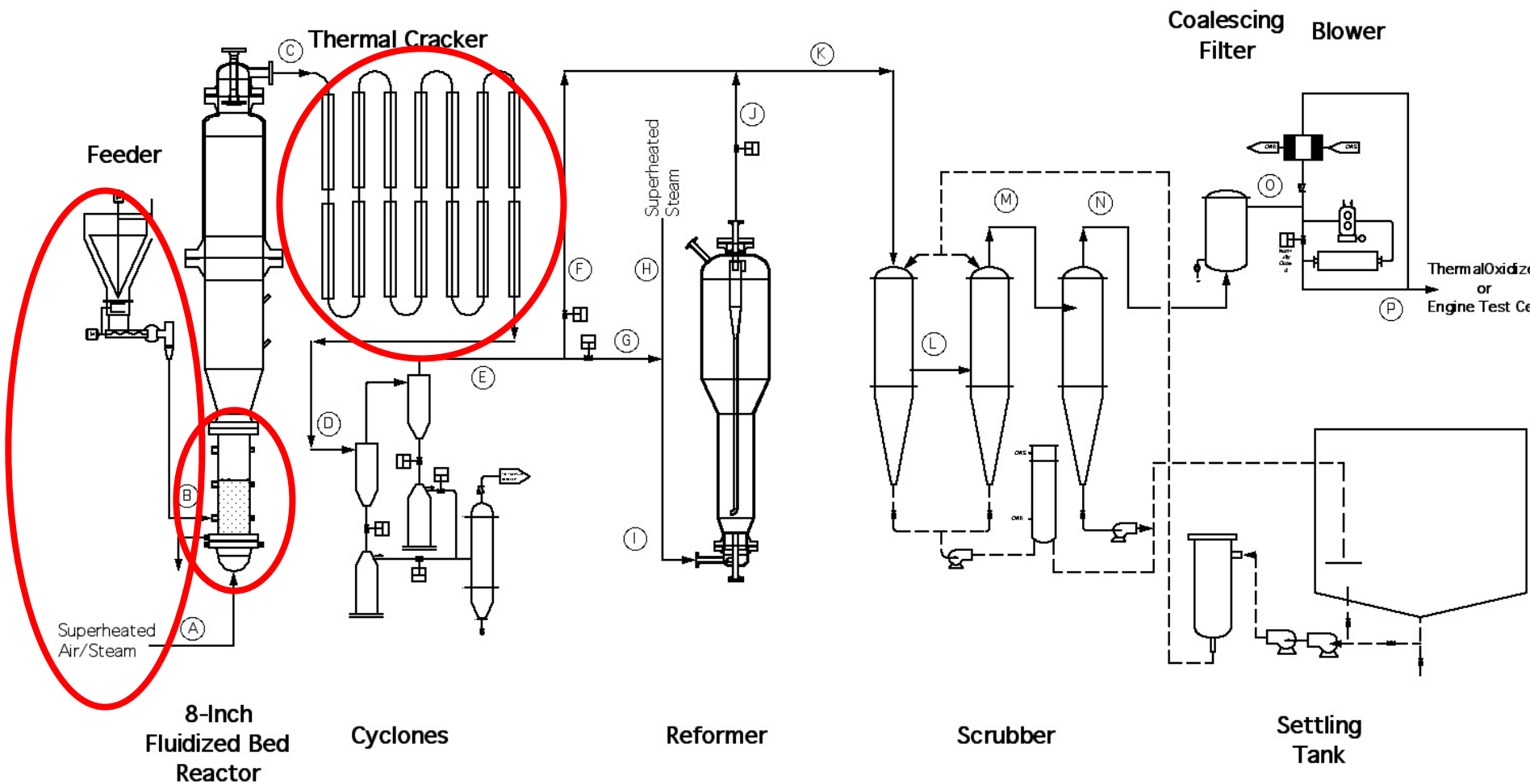
**8" Fluidized Bed  
Reactor**

**Catalytic  
Steam Reformer**



# NREL 150 kWt Thermochemical Pilot Development Unit

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# On-line Analytical Capabilities

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- Non-dispersive infrared (NDIR) Analyzer for CH<sub>4</sub> (range: 0-50 vol%)
- NDIR Analyzers for CO<sub>2</sub> and CO (0-50 vol% range)
- Paramagnetic Oxygen Analyzer (range of 0-25 vol%)
- H<sub>2</sub> thermal conductivity analyzer (range of 0-50 vol% and analog inputs for %CO, %CH<sub>4</sub> and %CO<sub>2</sub> to correct the H<sub>2</sub> value)
- Quad Micro Gas Chromatograph  
4 channel, on-line GC with 2-3 min cycle time  
H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub> paraffin's and olefins
- Transportable molecular beam mass spectrometer (TMBMS)  
Continuous, real-time monitoring of all gas phase products with particular emphasis on condensible tars and heteroatoms



# Baseline Parametric Corn Stover Gasification

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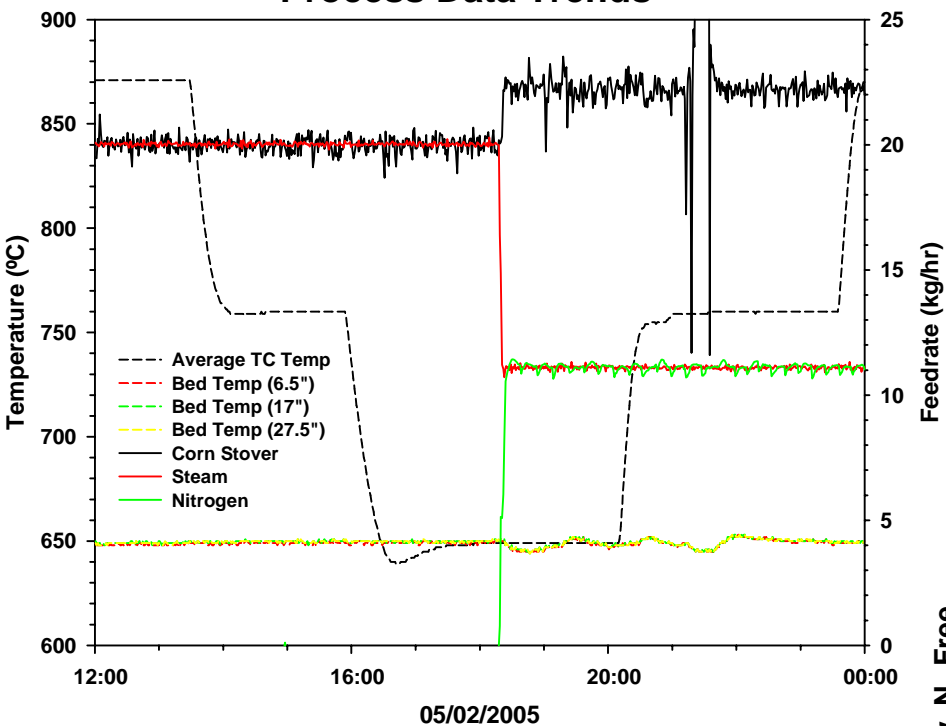
- Baseline data for Integrated Catalyst Studies subtask to evaluate 3 tar reforming catalysts in the next 3 months
- A total of 1633 kg of corn stover fed over a ~80 hour period; 1288 kg was fed during 56 continuous hours of statistically designed parametric gasification conditions
- 24 gasification conditions studied for process model development
  - Variables: bed and thermal cracker temperature and steam-to-biomass ratio
  - Desired results: carbon conversion (char yields), gas compositions, tar yields, tar composition, N and S release



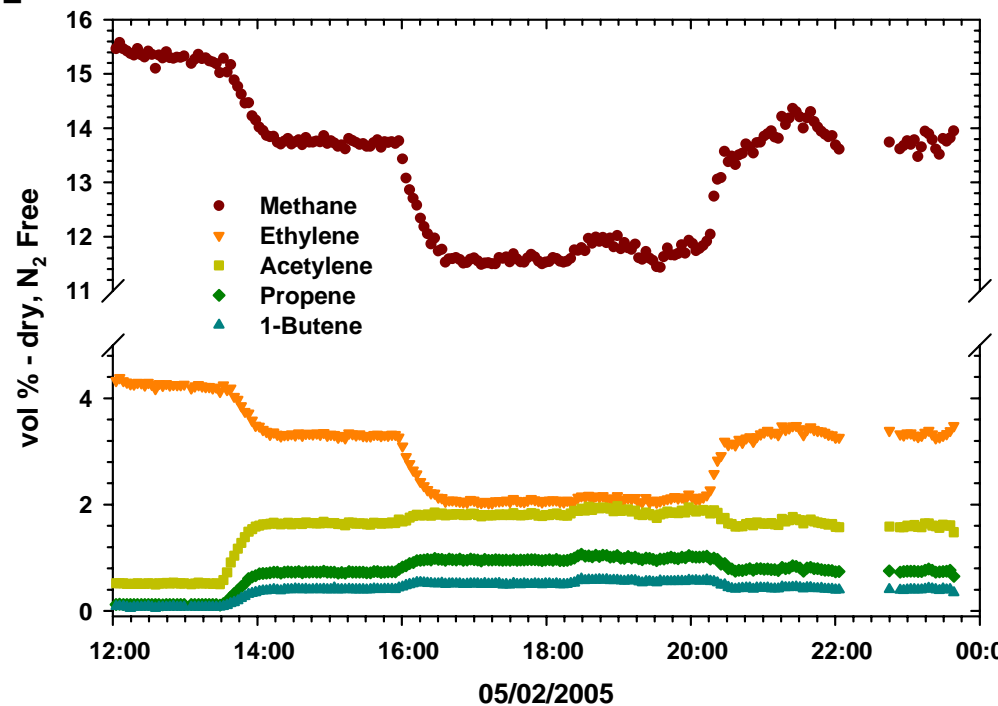
# Real-time data from corn stover gasification

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## Process Data Trends



## GC Gas Composition

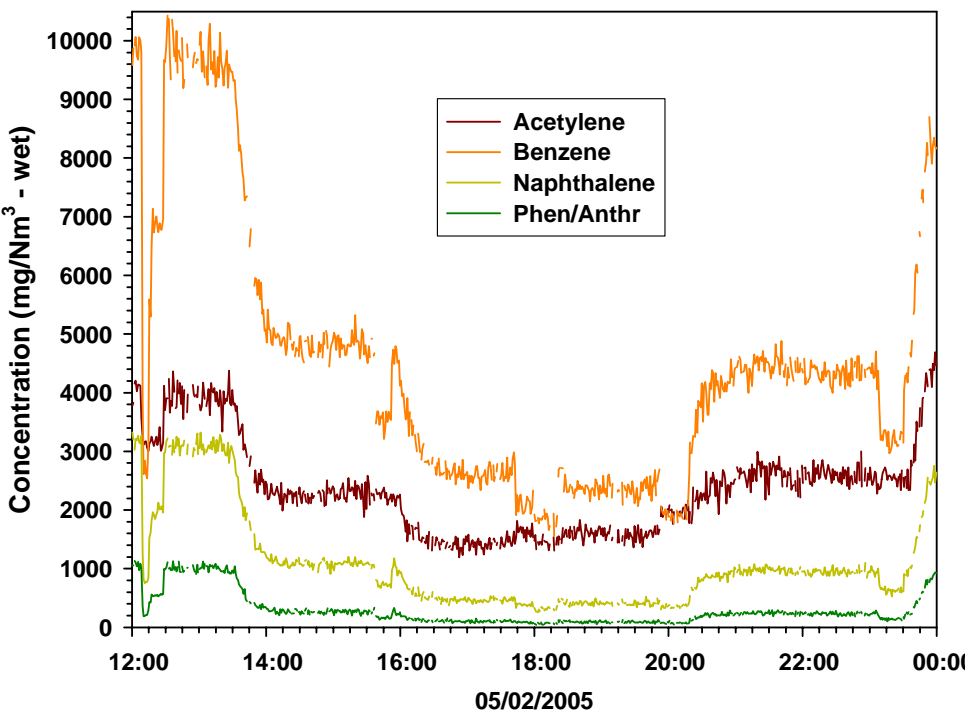




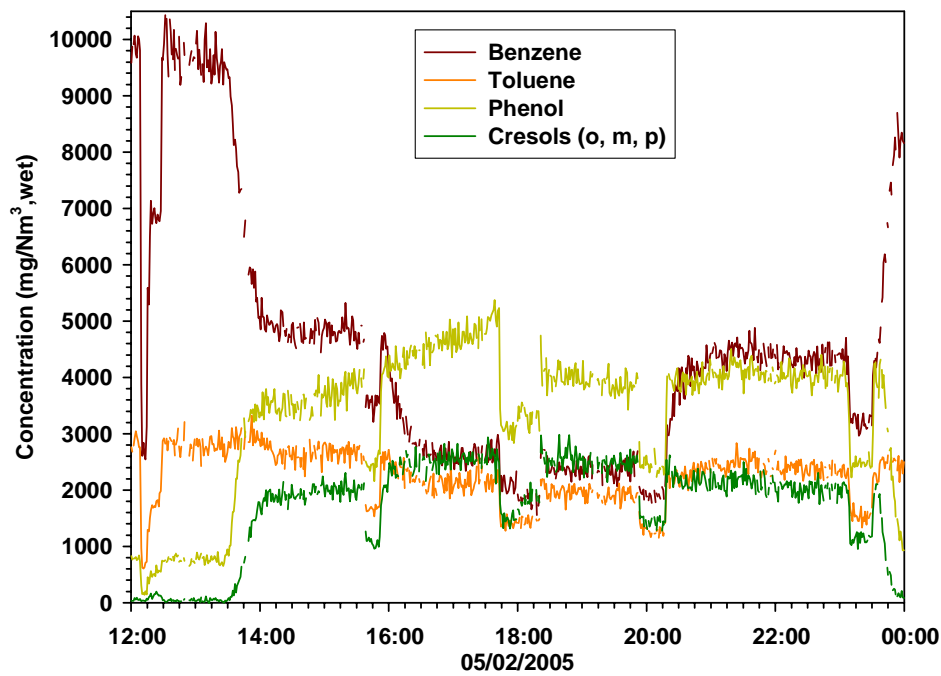
# On-line Tar Measurements

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**MBMS - Acetylene and Tertiary Tars**



**MBMS - Benzene and Secondary Tars**



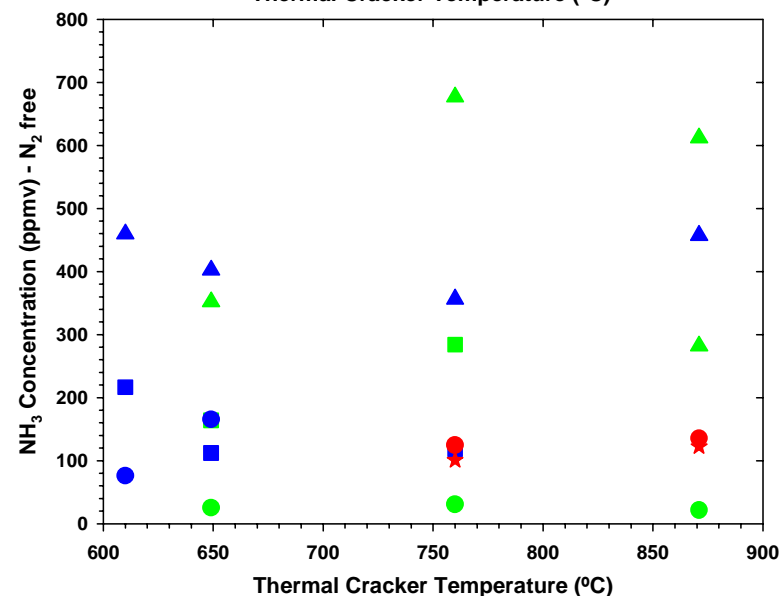
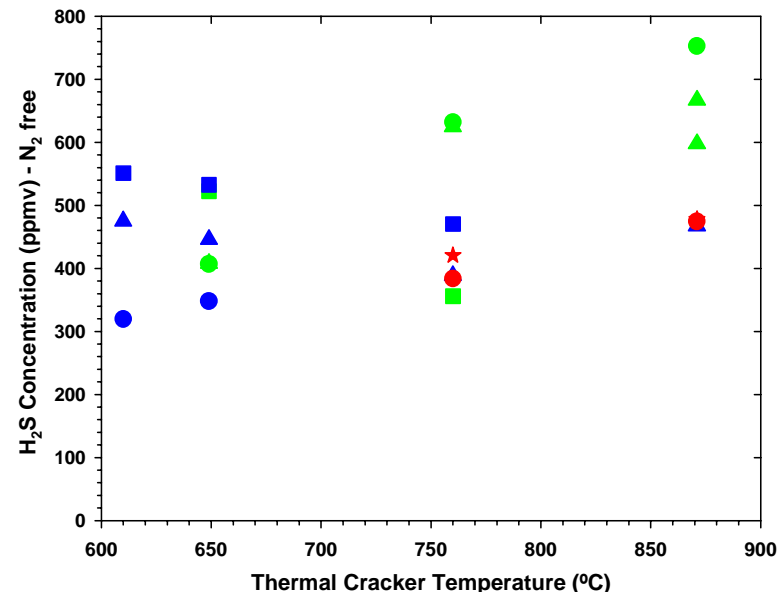
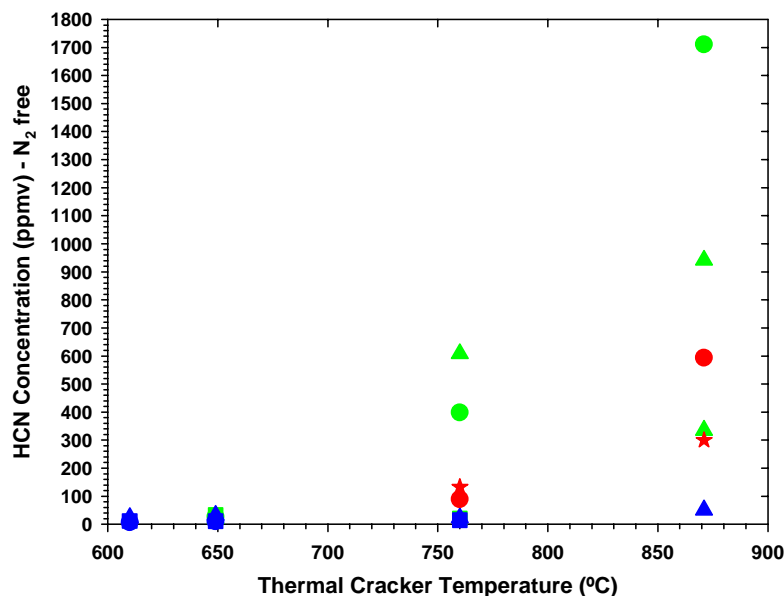


# Non-syngas Products

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### Draeger tube analysis of grab samples taken at each steady-state process condition

- Look for correlations with process conditions
- Need on-line measurement to pH of scrubber water to correlate with HCN/NH<sub>3</sub> solubility in water.
- Need on-line sulfur measurement capability with higher accuracy and precision.







# Summary of Results

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24 gasification conditions studied for process model development

- bed temperature – 593, 649, 715°C
- thermal cracker temperature – 610, 649, 760, 871°C
- steam-to-biomass ratio – 1, 0.5, 0.33

Continuous GC analysis for permanent gas composition (up to C4's)

- Average gas composition for each steady-state condition

Continuous tar monitoring with MBMS

- Quantified tars: benzene, toluene, phenol, naphthalene, phenanthrene/anthracene

30 solid samples collected for analysis

- 3 feed samples
- 25 char samples
- 2 bed samples

26 syngas grab samples

- offline H<sub>2</sub>S, HCN, and NH<sub>3</sub> analysis

ID	Biomass kg/hr	Steam kg/hr	N2 kg/hr	Bed Temp C	TC Temp C	Mass Closure (total)
CS_g1_1.1	20	20	0	649	871	94.2
CS_g1_1.2	20	20	0	649	760	99.0
CS_g1_1.3	20	20	0	649	649	107
CS_g1_2.1	22.2	11.1	11.1	649	649	105
CS_g1_2.2	22.2	11.1	11.1	649	760	106
CS_g1_2.3	22.2	11.1	11.1	649	871	103
CS_g1_3.1	27	9	13.5	649	871	101
CS_g1_3.2	27	9	13.5	649	760	100
CS_g1_3.3	27	9	13.5	649	649	100
CS_g1_3.4	27	9	13.5	593	649	99.0
CS_g1_3.5	27	9	13.5	593	610	100
CS_g1_3.8	27	9	13.5	593	871	98.3
CS_g1_1.4	20	20	0	593	649	99.2
CS_g1_1.5	20	20	0	593	610	102
CS_g1_2.4	22.2	11.1	11.1	593	610	101
CS_g1_2.5	22.2	11.1	11.1	593	649	108
CS_g1_2.6	22.2	11.1	11.1	593	760	99.6
CS_g1_4.1	15	9	12.5	715	871	99.9
CS_g1_3.7	15	11.1	11.1	715	760	105
CS_g1_1.6	15	15	7.5	715	760	103
CS_g1_1.7	15	15	7.5	715	871	104



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### **FY05**

- Completed parametric corn stover gasification studies for catalyst testing baseline
- Complete element balances pending solids analysis
- Multivariate analysis of corn stover gasification data to correlation gas composition with process conditions
- Complete bench-scale gasification of collected residues/feedstocks

### **FY06**

- Coordinate with NREL BioProcessing R&D Group (Sugars Platform) to generate enough biochemical conversion residues for full-stream catalyst testing in NREL TCPDU.
- Baseline parametric gasification of lignin-rich residues
- Continue bench-scale gasification studies and integrate with Gas Cleanup and Conditioning projects



# Critical Issues and Show-stoppers

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- Parametric Corn Stover Gasification studies reinforced the need for on-line (real-time) N and S measurements
  - $\text{NH}_3$  and HCN conversion over reforming catalyst
  - Impact of sulfur ( $\text{H}_2\text{S}$ ) on reforming catalyst performance
  - Evaluate commercial sulfur removal options (TC Analysis Project)
- High Ash Content of Biorefinery Residues
  - Catalytic effects?
  - Bed agglomeration vs. Temperature
  - Ash handling



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- Use pilot-scale data to develop publicly available correlations between process conditions and syngas yield, char yield and syngas composition as input for process simulations of integrated thermochemical processes.
- Provide a gasification test facility for integrated biorefinery developers
  - Corn Stover Residue (lignin) from NREL Biochemical PDU
  - Process residues of commercial interest
  - Commercial feedstocks in BC/TC pilot-scale integrated biorefinery
  - Validation of biorefinery residue gasification as a technology option for natural gas replacement in corn dry mills
- Highlights the impact of sulfur transformation in thermochemical processes
  - Baseline syngas quality data to evaluate future gas cleanup and conditioning requirements and options
- Funding History (\$K) FY04 - 327      FY05 - 400



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## NREL Thermochemical Group

Rich Bain - Group Manager

Daniel Carpenter – MBMS analytical support

Steve Deutch – analytical support

Calvin Feik – PDU operation

Rick French – MBMS analytical support

Steve Kelley – Area Leader

Ray Hanson – PDU operation

Steve Phillips – PDU operation

Matt Ratcliff – analytical support

Steve Thomas (NREL) and Richard Hess (INL) for corn  
stover procurement and processing